# An Improved United-Atom Force Field for 1-Alkyl-3-methylimidazolium chloride

Zhiping Liu[‡], Ting Chen, Alex Bell,* Berend Smit*
(*Energy Biosciences Institute and Department of Chemical Engineering, University of California, Berkeley, Berkeley, CA 94720-1462, USA*)
Email: alexbell@berkeley.edu, berend-smit@berkeley.edu
November 16, 2009

**Supporting information**: All the parameters of the force fields for [$C_n$mim][Cl] can be found in Table S1. The atom coordinates in the optimized geometries of monomers and dimers of [$C_1$mim][Cl] and [$C_2$mim][Cl] were given in Table S2 for reference. Figures S1 and S2 gave the similar results for [$C_2$mim][Cl], as those discussed in section 3 for [$C_1$mim][Cl]. The typical distributions of counter-ions around the center anion and cation were demonstrated by the snapshots in Figs. S3 and S4. Figure S5 gave a typical integral of correlation function to estimate the viscosity。

Table S1 Force field parameters in this work

Non-bonded

| | Lennard-Jones | | charges / \|e\| * | |
|---|---|---|---|---|
| Atom | σ / Å | ε / kcal.mol$^{-1}$ | [$C_1$mim][Cl] | [$C_n$mim][Cl] (n ≥ 2) |
| NA | 3.250 | 0.170 | 0.027 | 0.015 |
| CR | 3.400 | 0.086 | 0.005 | 0.00 |
| CW | 3.400 | 0.086 | -0.1734 | -0.16 |
| H5 | 1.247 | 0.030 | 0.1544 | 0.15 |
| H4 | 1.604 | 0.030 | 0.2188 | 0.20 |
| CN3 | 3.813 | 0.190 | 0.2543 | 0.26 |
| CN2 | 3.822 | 0.142 | 0.2543 | 0.23 |
| CT2 | 3.947 | 0.133 | - | 0.03* |
| CT3 | 3.902 | 0.185 | - | 0.00 |
| $Cl^-$ | 3.742 | 0.150 | -0.80 | -0.80 |

* The value is for CT2 connected with CN2. For other CT2, the charges are set to zero.

Bonds

| Bond | $k_r$ / kcal.mol$^{-1}$Å$^{-2}$ | $r_0$ / Å |
|---|---|---|
| NA-CR | 411.1 | 1.325 |
| CW-NA | 411.1 | 1.378 |
| CW-CW | 478.4 | 1.343 |
| CW-H4 | 344.3 | 1.070 |
| CR-H5 | 344.3 | 1.070 |
| NA-CN2 | 337.0 | 1.472 |
| CT2-CN2 | 310.0 | 1.526 |

Angles

| Angle | $k_\theta$ / kcal.mol$^{-1}$rad$^{-2}$ | $\theta_0$ / rad |
|---|---|---|
| CW-NA-CR | 67.8 | 108.0 |
| CW-NA-CN2 | 64.2 | 125.7 |
| CR-NA-CN2 | 64.2 | 126.3 |
| NA-CR-NA | 73.7 | 109.9 |
| NA-CR-H5 | 51.2 | 125.7 |
| CN3-NA-CW | 64.2 | 125.7 |
| CN3-NA-CR | 64.2 | 126.3 |
| CW-NA-CR | 67.8 | 108.0 |
| H4-CW-NA | 51.2 | 122.1 |
| H4-CW-CW | 50.0 | 130.7 |
| NA-CW-CW | 69.8 | 107.1 |
| CW-CW-H4 | 50.0 | 130.7 |
| CW-CW-NA | 69.8 | 107.1 |
| H4-CW-NA | 51.2 | 122.1 |
| CT2-CN2-NA | 80.0 | 112.2 |
| CT2-CT2-CN2 | 40.0 | 109.5 |

Dihedrals

| Dihedral | n | $k_\chi$ / kcal.mol$^{-1}$ | δ / degree |
|---|---|---|---|
| H4-CW-NA-CN3 | 2 | 1.5 | 180 |
| H4-CW-NA-CR | 2 | 2 | 180 |
| CW-CW-NA-CR | 2 | 12 | 180 |
| NA-CW-CW-H4 | 2 | 1.5 | 180 |
| NA-CW-CW-NA | 2 | 12 | 180 |
| CN3-NA-CR-NA | 2 | 2 | 180 |
| CN3-NA-CR-H5 | 2 | 1.5 | 180 |
| CW-NA-CR-NA | 2 | 12 | 180 |
| CW-NA-CR-H5 | 2 | 1.5 | 180 |
| CW-CW-NA-CR | 2 | 12 | 180 |
| CW-CW-NA-CN2 | 2 | 2 | 180 |
| H4-CW-NA-CR | 2 | 2 | 180 |
| H4-CW-NA-CN2 | 2 | 1.5 | 180 |
| NA-CR-NA-CW | 2 | 12 | 180 |
| NA-CR-NA-CN2 | 2 | 2 | 180 |
| H5-CR-NA-CW | 2 | 1.5 | 180 |
| H5-CR-NA-CN2 | 2 | 1.5 | 180 |
| CW-NA-CN2-CT2 | 1 | 0.694 | 0 |
| | 2 | 0.554 | 180 |
| | 3 | -0.564 | 0 |
| CR-NA-CN2-CT2 | 1 | 0.518 | 0 |
| | 2 | 0.046 | 180 |
| | 3 | -0.782 | 0 |
| X-CT2-CT2-X | 1 | 1.6 | 0 |
| | 2 | 0.6 | 180 |
| | 3 | 1 | 0 |

Table S2a Atom coordinates (unit: 0.1nm) in optimized geometry of [$C_1$mim][Cl] monomers at B3LYP/6-31G+(d,p) level

| | Atoms | X | Y | Z | | Atoms | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| | N | 1.309 | -0.832 | 0.000 | | N | -2.070 | -0.244 | 0.000 |
| | C | 0.145 | -0.165 | 0.000 | | C | -1.461 | 0.953 | 0.000 |
| | N | 0.423 | 1.146 | 0.000 | | N | -0.137 | 0.759 | 0.000 |
| | C | 1.796 | 1.322 | 0.000 | | C | 0.124 | -0.600 | 0.000 |
| | C | 2.357 | 0.078 | 0.000 | | C | -1.091 | -1.226 | 0.000 |
| | H | -0.908 | -0.560 | 0.000 | | H | -1.960 | 1.909 | 0.000 |
| | H | 2.252 | 2.299 | 0.000 | | H | 1.176 | -0.939 | 0.000 |
| | H | 3.390 | -0.230 | 0.000 | | H | -1.340 | -2.275 | 0.000 |
| **5m** | C | -0.610 | 2.193 | 0.000 | **4m** | C | 0.898 | 1.814 | 0.000 |
| | C | 1.422 | -2.292 | 0.000 | | C | -3.515 | -0.470 | 0.000 |
| | H | -1.585 | 1.692 | 0.000 | | H | 0.787 | 2.426 | -0.897 |
| | H | -0.501 | 2.809 | 0.895 | | H | 0.787 | 2.426 | 0.898 |
| | H | -0.501 | 2.809 | -0.895 | | H | 1.873 | 1.302 | 0.000 |
| | H | 0.416 | -2.712 | 0.000 | | H | -4.028 | 0.492 | 0.000 |
| | H | 1.955 | -2.623 | 0.894 | | H | -3.801 | -1.030 | 0.893 |
| | H | 1.955 | -2.623 | -0.894 | | H | -3.801 | -1.030 | -0.893 |
| | Cl | -2.897 | -0.581 | 0.000 | | Cl | 3.296 | -0.571 | 0.000 |
| | N | 1.129 | 1.088 | 0.000 | | N | 1.092 | -0.743 | 0.269 |
| | C | 1.917 | 0.000 | 0.000 | | C | 0.000 | -0.158 | 0.794 |
| | N | 1.129 | -1.088 | 0.000 | | N | -1.092 | -0.743 | 0.269 |
| | C | -0.194 | -0.682 | 0.000 | | C | -0.680 | -1.617 | -0.728 |
| | C | -0.194 | 0.682 | 0.000 | | C | 0.680 | -1.617 | -0.728 |
| | H | 2.995 | 0.000 | 0.000 | | H | 0.000 | 0.526 | 1.623 |
| | H | -1.066 | -1.326 | 0.000 | | H | -1.384 | -2.163 | -1.333 |
| | H | -1.067 | 1.325 | 0.000 | | H | 1.384 | -2.163 | -1.333 |
| **44** | C | 1.587 | -2.477 | 0.000 | **top** | C | -2.443 | -0.215 | 0.446 |
| | C | 1.587 | 2.478 | 0.000 | | C | 2.443 | -0.215 | 0.446 |
| | H | 2.678 | -2.498 | 0.000 | | H | -2.664 | -0.117 | 1.511 |
| | H | 1.213 | -2.984 | 0.892 | | H | -2.491 | 0.767 | -0.035 |
| | H | 1.213 | -2.984 | -0.892 | | H | -3.154 | -0.909 | -0.004 |
| | H | 2.677 | 2.498 | 0.000 | | H | 2.664 | -0.117 | 1.511 |
| | H | 1.212 | 2.984 | 0.892 | | H | 2.491 | 0.767 | -0.035 |
| | H | 1.212 | 2.985 | -0.891 | | H | 3.154 | -0.908 | -0.004 |
| | Cl | -3.240 | 0.000 | 0.000 | | Cl | 0.000 | 2.215 | -0.415 |

Table S2a Atom coordinates (unit: 0.1nm) in optimized geometry of [$C_2$mim][Cl] monomers at B3LYP/6-31G+(d,p) level

| | Atoms | X | Y | Z | | Atoms | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| **5e** | N | -0.251 | 0.912 | -0.286 | **5m** | N | 1.293 | 0.405 | -0.166 |
| | C | -0.352 | -0.403 | -0.048 | | C | 0.097 | -0.201 | -0.118 |
| | N | -1.655 | -0.702 | 0.075 | | N | 0.305 | -1.514 | 0.041 |
| | C | -2.405 | 0.454 | -0.088 | | C | 1.667 | -1.759 | 0.091 |
| | C | -1.520 | 1.468 | -0.313 | | C | 2.289 | -0.552 | -0.042 |
| | H | 0.545 | -1.078 | 0.006 | | H | -0.932 | 0.246 | -0.169 |
| | H | -3.482 | 0.456 | -0.035 | | H | 2.072 | -2.750 | 0.221 |
| | H | -1.686 | 2.518 | -0.492 | | H | 3.337 | -0.297 | -0.054 |
| | C | -2.171 | -2.047 | 0.333 | | C | -0.785 | -2.495 | 0.151 |
| | C | 1.041 | 1.612 | -0.466 | | C | 1.485 | 1.857 | -0.373 |
| | C | 1.404 | 2.464 | 0.748 | | C | 0.564 | 2.696 | 0.509 |
| | H | -2.825 | -2.357 | -0.485 | | H | -0.701 | -3.026 | 1.101 |
| | H | -1.324 | -2.731 | 0.398 | | H | -1.729 | -1.942 | 0.110 |
| | H | -2.723 | -2.060 | 1.275 | | H | -0.724 | -3.202 | -0.680 |
| | H | 0.956 | 2.216 | -1.374 | | H | 1.312 | 2.069 | -1.433 |
| | H | 1.785 | 0.823 | -0.624 | | H | 2.537 | 2.060 | -0.157 |
| | H | 1.519 | 1.836 | 1.636 | | H | 0.758 | 2.508 | 1.569 |
| | H | 2.362 | 2.959 | 0.562 | | H | 0.750 | 3.755 | 0.307 |
| | H | 0.655 | 3.237 | 0.952 | | H | -0.492 | 2.491 | 0.306 |
| | Cl | 2.446 | -1.681 | -0.078 | | Cl | -2.899 | 0.505 | -0.091 |
| **4e** | N | -0.225 | 0.485 | -0.257 | **4m** | N | 1.637 | 0.022 | -0.336 |
| | C | -1.525 | 0.777 | -0.359 | | C | 0.946 | 1.149 | -0.102 |
| | N | -2.239 | -0.300 | 0.006 | | N | -0.356 | 0.852 | -0.043 |
| | C | -1.350 | -1.308 | 0.354 | | C | -0.521 | -0.508 | -0.244 |
| | C | -0.085 | -0.818 | 0.191 | | C | 0.731 | -1.025 | -0.425 |
| | H | -1.938 | 1.718 | -0.685 | | H | 1.376 | 2.132 | 0.015 |
| | H | -1.691 | -2.279 | 0.674 | | H | -1.542 | -0.930 | -0.214 |
| | H | 0.932 | -1.237 | 0.292 | | H | 1.050 | -2.038 | -0.611 |
| | C | -3.698 | -0.398 | 0.019 | | C | -1.460 | 1.807 | 0.183 |
| | C | 0.902 | 1.410 | -0.543 | | C | 3.102 | -0.086 | -0.426 |
| | C | 1.335 | 2.176 | 0.703 | | C | 3.725 | -0.693 | 0.831 |
| | H | -4.043 | -0.633 | 1.028 | | H | -1.277 | 2.353 | 1.110 |
| | H | -4.124 | 0.556 | -0.292 | | H | -1.519 | 2.496 | -0.662 |
| | H | -4.023 | -1.179 | -0.671 | | H | -2.385 | 1.213 | 0.256 |
| | H | 0.566 | 2.075 | -1.344 | | H | 3.487 | 0.921 | -0.610 |
| | H | 1.727 | 0.772 | -0.887 | | H | 3.328 | -0.689 | -1.310 |
| | H | 1.724 | 1.481 | 1.452 | | H | 3.350 | -1.704 | 1.013 |
| | H | 2.150 | 2.854 | 0.432 | | H | 4.810 | -0.750 | 0.707 |
| | H | 0.519 | 2.769 | 1.132 | | H | 3.510 | -0.082 | 1.712 |
| | Cl | 3.057 | -1.131 | -0.093 | | Cl | -3.664 | -0.760 | 0.138 |

Table S2c Atom coordinates (unit: 0.1nm) in optimized geometry of [$C_1$mim][Cl] dimer at B3LYP/6-31G+(d,p) level

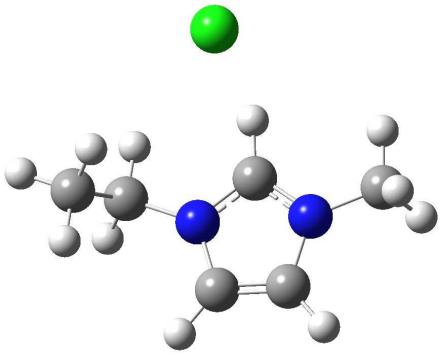
| | Atoms | X | Y | Z | Atom type |
|---|---|---|---|---|---|
| 1 | N1 | 3.067 | -0.357 | 0.198 | NA |
| 2 | C1 | 2.206 | -0.212 | -0.819 | CR |
| 3 | N2 | 1.534 | -1.361 | -0.967 | NA |
| 4 | C2 | 1.965 | -2.265 | -0.012 | CA |
| 5 | C3 | 2.938 | -1.638 | 0.711 | CA |
| 6 | H1 | 2.009 | 0.739 | -1.316 | H5 |
| 7 | H2 | 1.489 | -3.225 | 0.109 | H4 |
| 8 | H3 | 3.522 | -1.980 | 1.551 | H4 |
| 9 | C4 | 0.484 | -1.612 | -1.959 | CT |
| 10 | C5 | 3.961 | 0.704 | 0.677 | CT |
| 11 | H4 | 0.194 | -0.658 | -2.401 | H1 |
| 12 | H5 | 0.868 | -2.276 | -2.738 | H1 |
| 13 | H6 | -0.361 | -2.076 | -1.437 | H1 |
| 14 | H7 | 3.535 | 1.664 | 0.370 | H1 |
| 15 | H8 | 4.960 | 0.572 | 0.253 | H1 |
| 16 | H9 | 4.014 | 0.654 | 1.766 | H1 |
| 17 | N3 | -3.067 | 0.357 | -0.198 | NA |
| 18 | C6 | -2.206 | 0.212 | 0.819 | CR |
| 19 | N4 | -1.534 | 1.361 | 0.967 | NA |
| 20 | C7 | -1.965 | 2.265 | 0.012 | CA |
| 21 | C8 | -2.938 | 1.638 | -0.711 | CA |
| 22 | H10 | -2.009 | -0.739 | 1.316 | H5 |
| 23 | H11 | -1.489 | 3.225 | -0.109 | H4 |
| 24 | H12 | -3.522 | 1.980 | -1.551 | H4 |
| 25 | C9 | -0.484 | 1.612 | 1.959 | CT |
| 26 | C10 | -3.961 | -0.704 | -0.677 | CT |
| 27 | H13 | -0.868 | 2.276 | 2.738 | H1 |
| 28 | H14 | -0.194 | 0.658 | 2.401 | H1 |
| 29 | H15 | 0.361 | 2.076 | 1.437 | H1 |
| 30 | H16 | -3.535 | -1.664 | -0.370 | H1 |
| 31 | H17 | -4.014 | -0.654 | -1.766 | H1 |
| 32 | H18 | -4.960 | -0.572 | -0.253 | H1 |
| 33 | Cl1 | -1.406 | -2.883 | 0.675 | Cl |
| 34 | Cl2 | 1.406 | 2.883 | -0.675 | Cl |

Table S2d Atom coordinates (unit: 0.1nm) in optimized geometry of [$C_2$mim][Cl] dimer at B3LYP/6-31G+(d,p) level

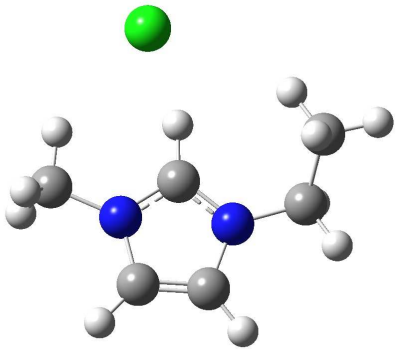
| | Atoms | X | Y | Z | Atom type |
|---|---|---|---|---|---|
| 1 | N1 | -3.411 | 0.841 | 0.130 | NA |
| 2 | C1 | -2.531 | 0.264 | -0.702 | CR |
| 3 | N2 | -1.574 | 1.156 | -0.985 | NA |
| 4 | C2 | -1.833 | 2.336 | -0.310 | CA |
| 5 | C3 | -2.989 | 2.140 | 0.387 | CA |
| 6 | H1 | -2.489 | -0.793 | -0.974 | H5 |
| 7 | H2 | -1.135 | 3.160 | -0.334 | H4 |
| 8 | H3 | -3.532 | 2.797 | 1.047 | H4 |
| 9 | C4 | -0.432 | 0.902 | -1.871 | CT |
| 10 | C5 | -4.553 | 0.169 | 0.783 | CT |
| 11 | C6 | -5.062 | -1.038 | 0.002 | CT |
| 12 | H4 | -0.284 | -0.179 | -1.926 | H1 |
| 13 | H5 | -0.644 | 1.302 | -2.866 | H1 |
| 14 | H6 | 0.440 | 1.401 | -1.436 | H1 |
| 15 | H7 | -5.334 | 0.926 | 0.894 | H1 |
| 16 | H8 | -4.229 | -0.133 | 1.785 | H1 |
| 17 | H9 | -5.923 | -1.456 | 0.532 | HC |
| 18 | H10 | -5.388 | -0.752 | -1.003 | HC |
| 19 | H11 | -4.301 | -1.821 | -0.075 | HC |
| 20 | N3 | 3.410 | -0.841 | -0.131 | NA |
| 21 | C7 | 2.531 | -0.264 | 0.702 | CR |
| 22 | N4 | 1.574 | -1.156 | 0.985 | NA |
| 23 | C8 | 1.833 | -2.336 | 0.310 | CA |
| 24 | C9 | 2.989 | -2.140 | -0.387 | CA |
| 25 | C10 | 5.062 | 1.038 | -0.003 | CT |
| 26 | H12 | 2.488 | 0.793 | 0.973 | H5 |
| 27 | H13 | 1.135 | -3.161 | 0.334 | H4 |
| 28 | H14 | 3.532 | -2.797 | -1.047 | H4 |
| 29 | C11 | 0.432 | -0.902 | 1.871 | CT |
| 30 | C12 | 4.552 | -0.169 | -0.783 | CT |
| 31 | H15 | 0.644 | -1.302 | 2.866 | H1 |
| 32 | H16 | 0.284 | 0.178 | 1.927 | H1 |
| 33 | H17 | -0.440 | -1.401 | 1.436 | H1 |
| 34 | H18 | 4.229 | 0.133 | -1.785 | H1 |
| 35 | H19 | 5.334 | -0.926 | -0.894 | H1 |
| 36 | H20 | 5.388 | 0.752 | 1.003 | HC |
| 37 | H21 | 5.923 | 1.456 | -0.532 | HC |
| 38 | H22 | 4.300 | 1.821 | 0.075 | HC |
| 39 | Cl1 | 1.535 | 2.754 | 0.408 | Cl |
| 40 | Cl2 | -1.535 | -2.754 | -0.408 | Cl |

Table S3 Atom charges of [$C_n$mim][Cl] (n=1,3) by RESP fitting of ion-pair dimers

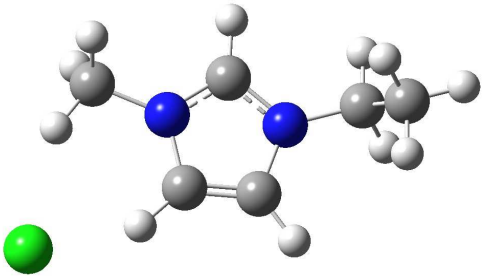
| | [$C_1$mim][Cl] | [$C_2$mim][Cl] | [$C_3$mim][Cl] |
|---|---|---|---|
| NA | 0.0343 | 0.0206 | 0.0348 |
| CR | -0.0031 | 0.0151 | -0.0553 |
| NA(m) | 0.0343 | -0.0134 | 0.0854 |
| CW(m) | -0.1620 | -0.0936 | -0.1756 |
| CW | -0.1620 | -0.2054 | -0.1508 |
| H5 | 0.1375 | 0.1249 | 0.1563 |
| H4(m) | 0.1909 | 0.1821 | 0.2037 |
| H4 | 0.1909 | 0.1889 | 0.1760 |
| CT | 0.2219 | 0.2394 | 0.2072 |
| CT | 0.2219 | 0.2075 | 0.1949 |
| CT | | 0.0373 | 0.0717 |
| CT | | | -0.0263 |
| Cl | -0.7046 | -0.7035 | -0.7221 |



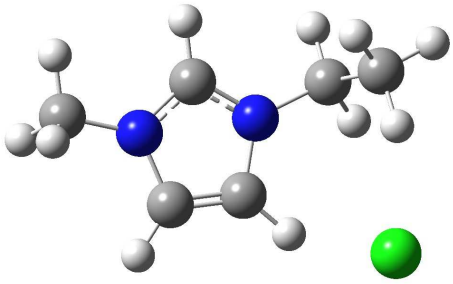
**5e** (-0.723)



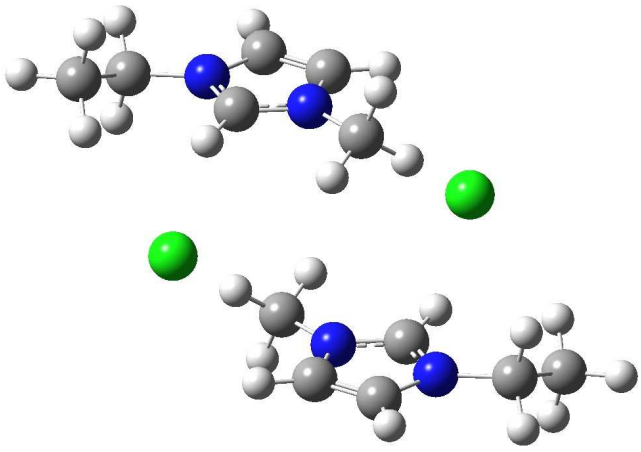
**5m** (-0.751)



**4m** (-0.824)

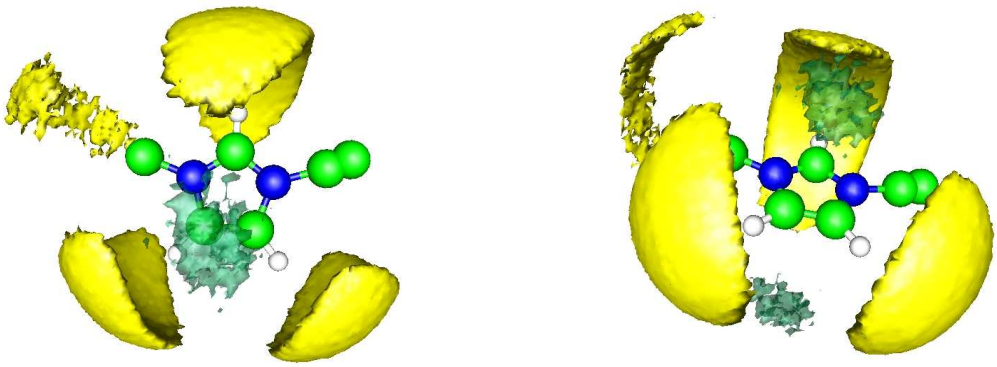


**4e** (-0.662)



**dimer**

Figure S1. Four optimized isomers for [$C_2$mim][Cl] ion pair and its dimers, obtained by ab initio calculation at B3LYP/6-31+G(d,p) level. The charges on chloride are shown as the numbers in bracket.



a. b

Figure S2. Three-dimensional probability distributions of chloride (yellow) and CR on cations (green) around cations in ionic liquid [$C_2$mim][Cl]. Density levels correspond to five and three times the bulk density for anions and cations, respectively. Two different views are shown in a and b.

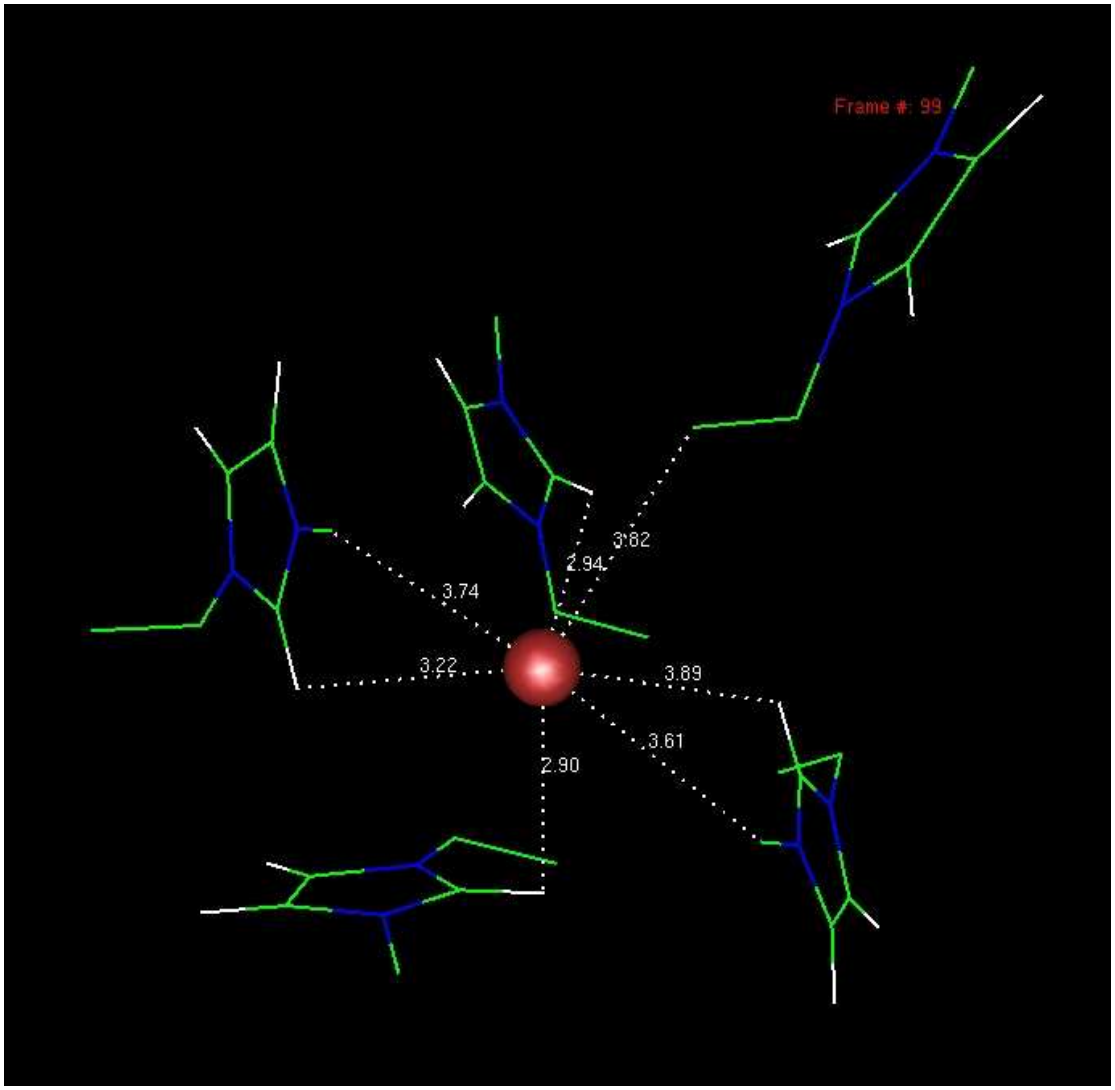


Figure S3. Typical coordination of cations around chloride in [$C_2$mim][Cl]. Some short distances between chloride and hydrogen/carbon in cations are shown.

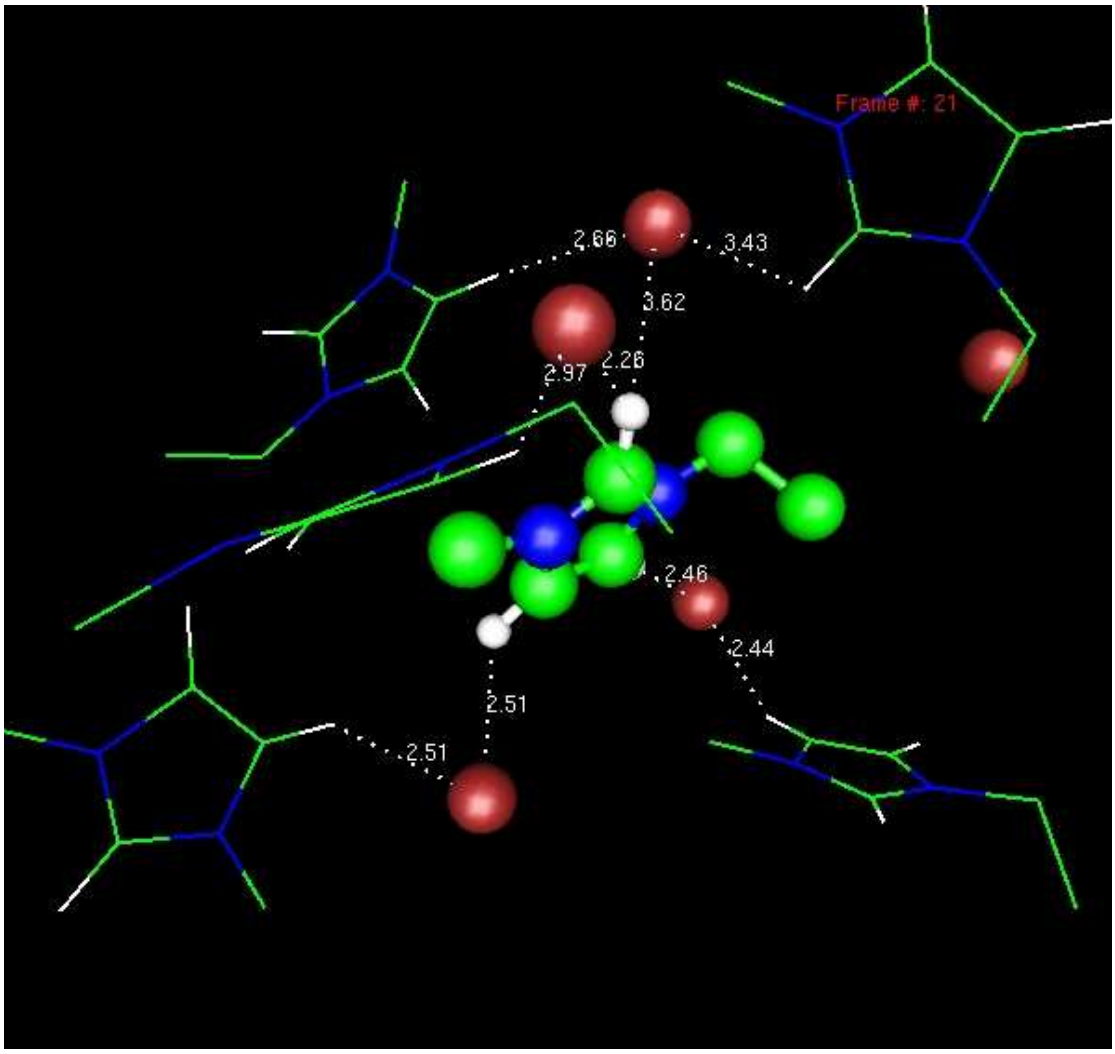



Figure S4. Typical coordination of choloride and cations around $[C_2mim]^+$ in $[C_2mim][Cl]$. Some short distances between chloride and hydrogen/carbon in cations are shown.

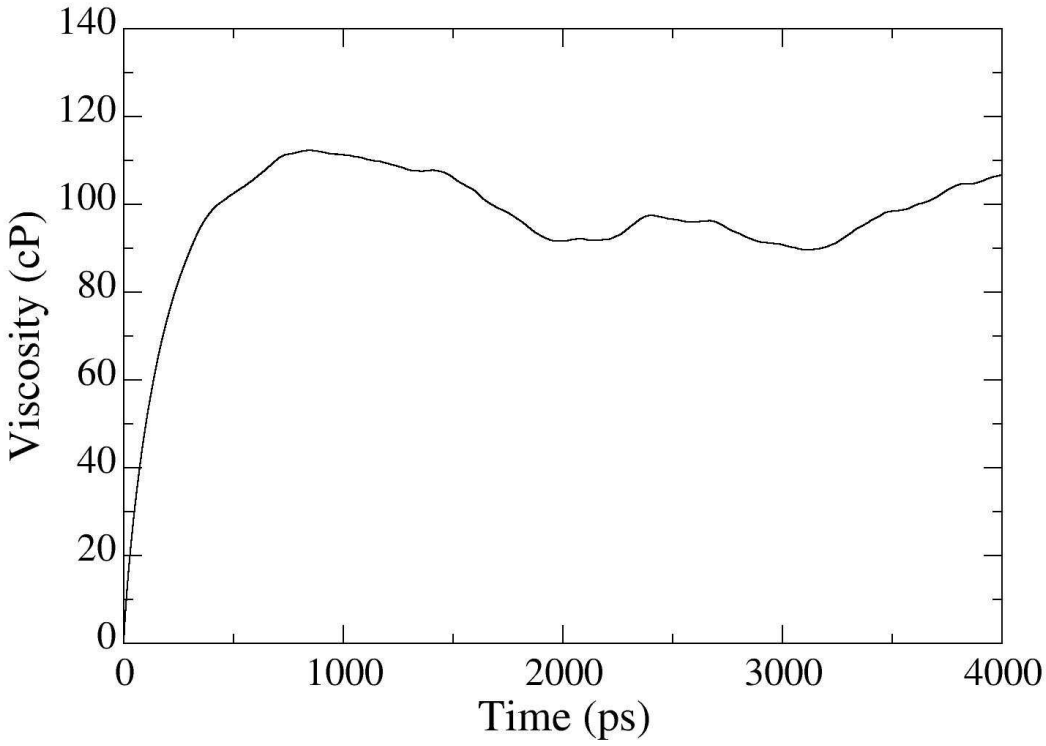



Figure S5 Viscosity of [$C_2$mim][Cl] at 353 K calculated by equation 6 in section 3.2.4.